

Supporting Information

Fabrication of sub-5 nm uniform zirconium oxide films on corrugated copper substrates by a scalable polymer brush assisted deposition method

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Substrate cleaning and sample activation: Interfacial Cu₂O, and CuO oxide layer is reduced to metallic copper by citric acid treatment. A few minutes of citric acid cleaning is sufficient for ashing the oxide layer and removing impurities from the surface. After the citric acid treatment, these samples were thoroughly washed in water to get rid of residual acid. Subsequent polymer brush deposition and annealing processes yield homogeneous polymer films.

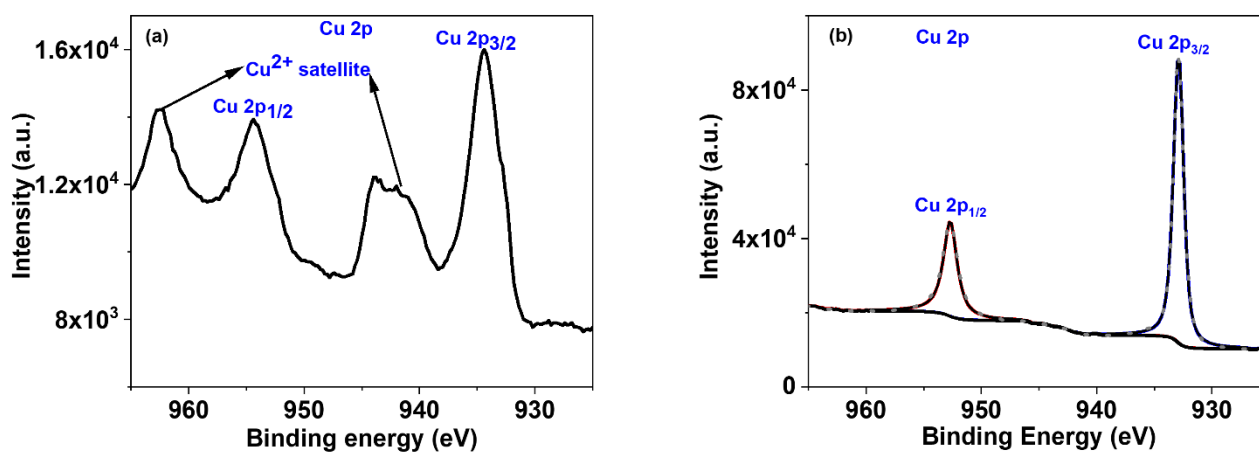


Figure S1 high resolution XPS spectra of Cu 2p of (a) blanket copper substrate and (b) post-citric acid treated sample (5 min).

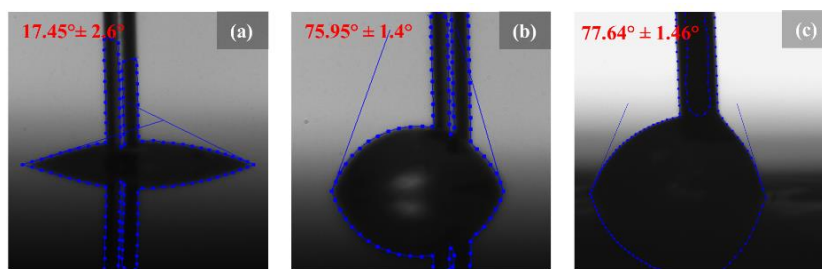


Figure S2 Advancing water contact angle of the a) citric acid treated substrate, b) PMMA brush coated substrate, and c) pressed homopolymer pellet.

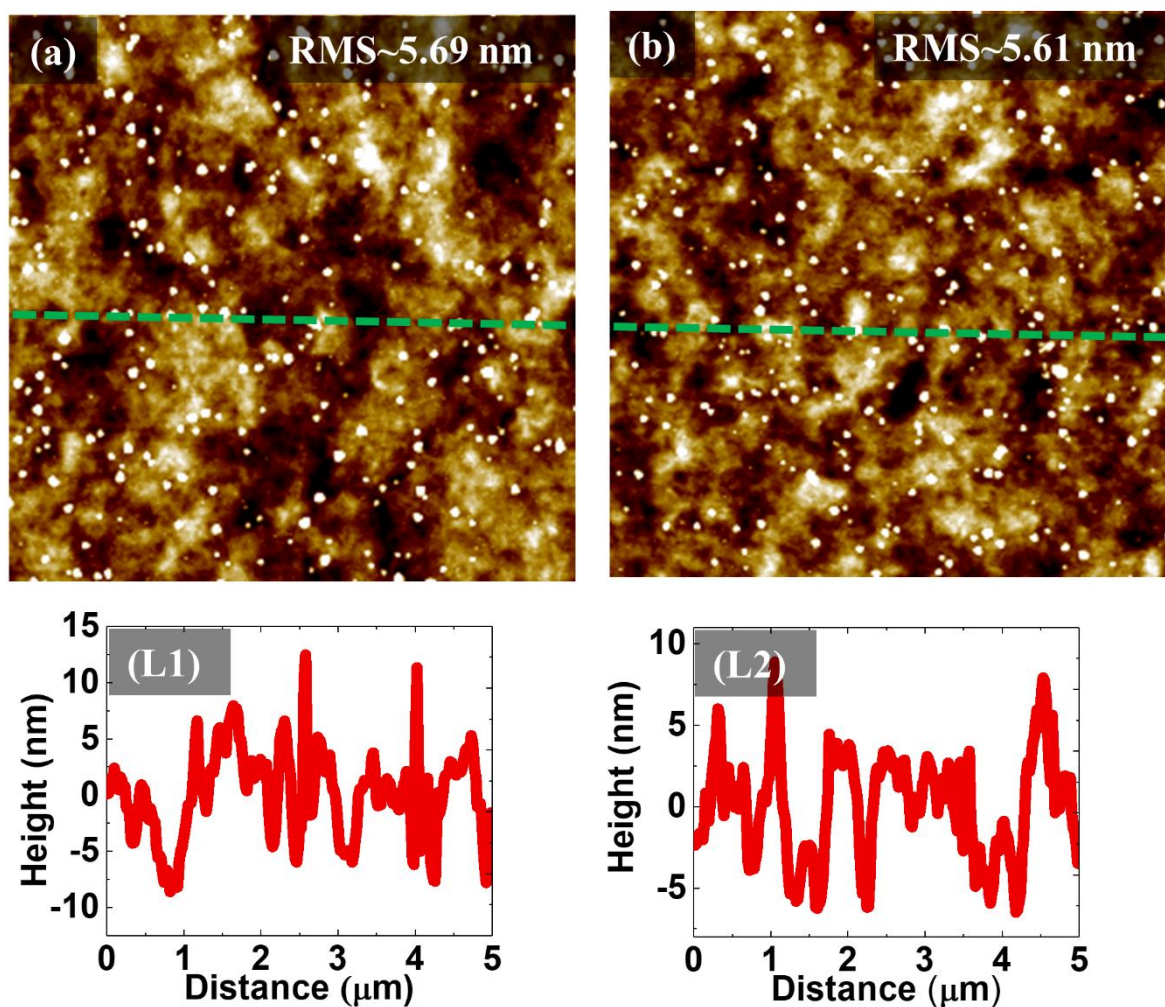


Figure S3 AFM images of the copper substrate (a) as received Cu sample and corresponding line images at L1 (b) toluene washed substrate and respective line image at L2.

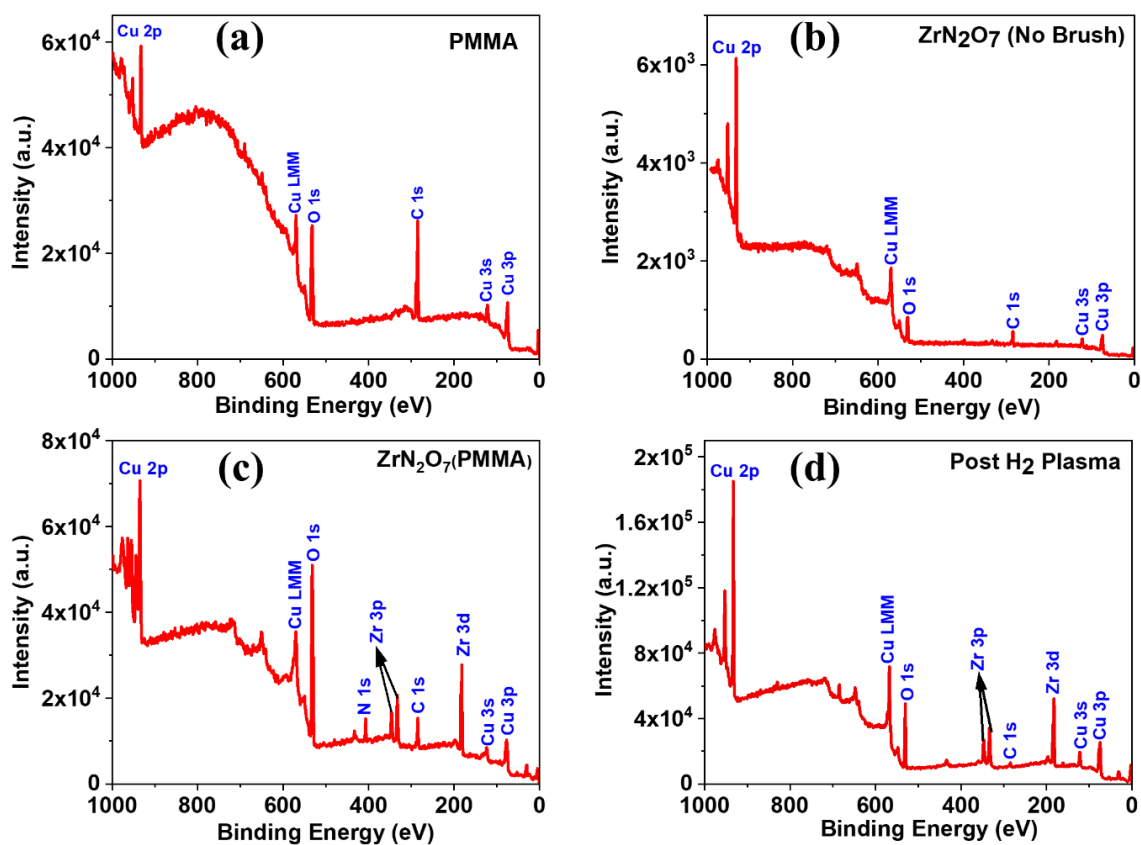


Figure S4 Wide energy XPS survey spectrum of (a) a grafted PMMA-SH brush on the copper substrate (b) an infiltrated zirconium oxynitrate with no brush (c) a spin deposited zirconium oxynitrate on PMMA brush and (d) a post reductive H₂ plasma annealed substrate.

Table S1: The peaks observed in XPS and their corresponding elements.

Binding Energy (eV)	element
29.7	Zr 4p
74.1	Cu 3p
121.6	Cu 3s
183	Zr 3d
284.8	C 1s
333	Zr 3p _{3/2}
346	Zr 3p _{1/2}
407	N 1s
431	Zr 3s
531.8	O 1s
566.8	Cu (LMM)
931.6	Cu 2p _{3/2}
951	Cu 2p _{1/2}

Table S2 The atomic weight percentage of respective elements in each sample evaluated from XPS.

At%	C 1s	O 1s	N 1s	Zr 3d	Cu 2p
PMMA	69.1	28.9	--	--	2.0
ZrN ₂ O ₇ (No Brush))	46.9		0.4	0.6	18.2
ZrN ₂ O ₇ (PMMA)	22.2	60.3	2.1	5.6	9.8
Post H ₂ plasma	12.0	51.7	--	19.0	17.3

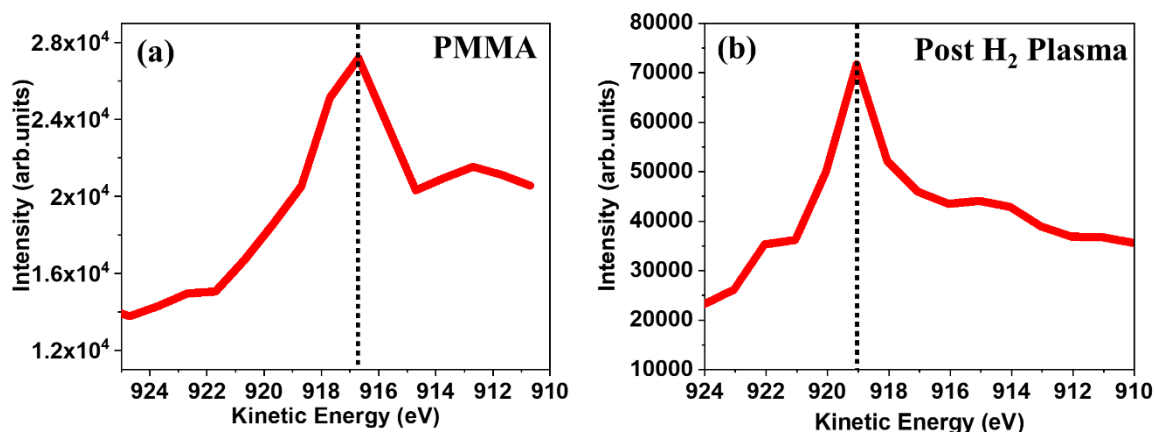


Figure S5 Cu (LMM) spectra extracted from survey spectra for (a) a PMMA brush grafted and (b) a post H₂ plasma sample.

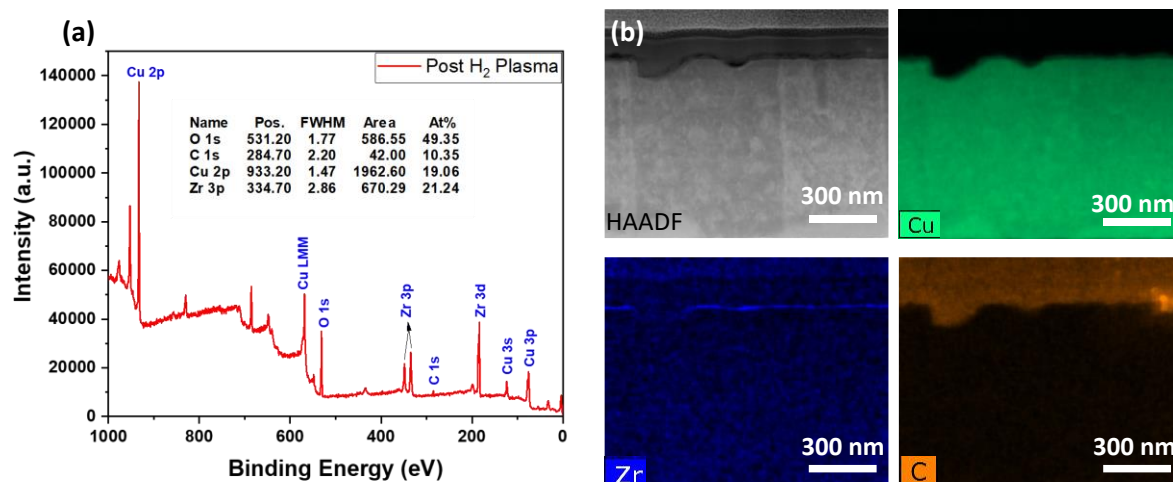


Figure S6 (a) Wide energy XPS survey spectrum and (b) STEM high-angle annular dark field (HAADF) and EDX maps of (Cu, Zr, and C,) images of H₂ plasma annealed infiltrated sample.